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Examination of Molecular Interaction Sites of Acetanilides with Organic Matter Surrogates Using Nuclear Magnetic Resonance Techniques

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The dynamics of acetanilide pesticide interactions with organic matter (OM) surrogates were examined using nuclear magnetic resonance (NMR) spectroscopy. Differences in the relative changes in ^{13}C and ^{1}H spin−lattice relaxation times (T_1) were measured at multiple molecular sites of metolachlor and the probe compound acetanilide to identify interaction sites and/or surfaces between the molecules and dissolved and colloidal OM surrogates. The decrease in T_1 at specific sites of acetanilide molecules was a function of the OM used and its concentration. High-affinity interactions at nonaromatic sites of metolachlor and acetanilide were observed with cellulose, chitin, and collagen, but interactions with lignin occurred with less site specificity and involved both aromatic and nonaromatic sites of the molecules. Changes in relaxation were compared to calculated and experimentally determined binding coefficients (K_{oc}). The T_1 relaxation of the aromatic sites of acetanilides showed better relations with K_{oc} than the nonaromatic sites. This study shows that NMR relaxation measurements can identify the high-affinity molecular interaction sites of acetanilides to OM surrogates.

KEYWORDS: Metolachlor; acetanilide; organic surrogates; binding sites; NMR

INTRODUCTION

Pesticides and other xenobiotic organic pollutants interact with soil surfaces and solution constituents through covalent and noncovalent interactions with varying degrees of affinity. The extent to which the different interaction mechanisms contribute to the retention of pollutants depends on both the sorbate and the sorbent properties. Sorption of nonpolar (hydrophobic) organic compounds (HOCs) has been described in terms of nonspecific hydrophobic partitioning (*1*−*3*). However, studies have shown that interactions other than van der Waals interactions are possible between pollutants and organic matter (OM). For example, the linear partition theory has been shown to inadequately describe the sorption/desorption process for pesticides (*4*) and other organic pollutants (*5*, *6*). Interaction mechanisms between organic pollutants and OM sorbents can vary due to the identity of their functional groups, acid−base character, polarity and polarizability, charge distribution, water solubility, hydrophobicity, configuration, and conformation (*7*−*11*). Specific molecular interactions of an individual sorbate structure with different sorbents can result in changes in the sorbate molecular conformations and orientations at the exposed macromolecular surfaces. Knowledge of these interactions is critical in understanding a sorbed pollutant's availability (desorption) and susceptibility to biodegradation and also in modeling pollutant fate.

Covalent and non-covalent interactions of HOCs with dissolved OM have been probed, using solution phase ^{13}C, ^{19}F, and ^{2}H NMR (*12*−*16*). Specific NMR parameters, such as spin−lattice relaxation (T_1 relaxation), line broadening, coupling constants, and chemical shifts of specific nuclei, can provide molecular information on the predominant sites and the interaction mechanisms between organic pollutants and environmental matrices. Spin−lattice relaxation (T_1 relaxation) is the process of energy exchange between individual nuclear spins and the surrounding liquid or solid lattice. When molecules interact with the organic phases, the interaction can induce changes to the T_1 relaxation times of the molecule. The T_1 measured is an average of the T_1 values of those nuclei associated with binding and those unassociated with the site. Bound sites will have a shorter relaxation time than the nonbound sites.

In a recent study, ^{1}H NMR relaxation of water in porous media was measured to detect the influence of sorbed hydrocarbons (*17*). Researchers have used T_1 relaxation measurements to quantify association (*18*) and to determine non-covalent interactions of molecules such as phenol, acenaphthenone, and F-acetonaphthone with humic acids by measuring the relaxation at a single labeled site in the molecule (e.g., the carbonyl carbon of acenaphthenone) (*14*, *15*). Ross and Biros (*19*) calculated the spin−spin (transverse) relaxation times (T_2 relaxation) of DDT to determine its preferential interaction sites with proteins.

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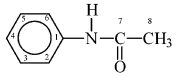
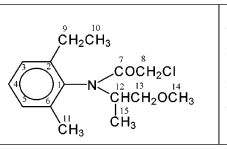
Table 1. Physical and Chemical Properties of Acetanilide and Metolachlor (*20*, *21*)

Chemical	Structure	Properties
Acetanilide		Mol. Weight 135.2 Physical state solid Solubility (mgL^{-1}) 5400 Log K_{ow} 1.37 Mol. surface area[a] $(A^0)^2$ 165.8
^{1}H NMR chemical shifts (ppm): H(2) –H(6) 6.9-7.7; H(8) 2.1 ^{13}C NMR chemical shifts (ppm): C(1) 138.6; C(2,6) 120.0; C(3,5) 128.7; C(4) 123.8; C(7) 169.2 ppm C(8) 24.05		
Metolachlor		Mol. Weight 283.8 Physical state liquid Solubility (mgL^{-1}) 530 Log K_{ow} 2.93 Mol. surface area[a] $(A^0)^2$ 327.9
^{1}H NMR chemical shifts (ppm): H(3) 7.34; H(5) 7.38; H(4) 7.28; H(8) 3.75; H(9) 2.52; H(10) 1.26; H(11) 2.20; H(12) 4.32; H(13) 3.65; H(14) 3.25 H(15)1.11		

[a] Molecular surface area was calculated using HyperChem.

The current study uses ^{1}H and ^{13}C NMR T_1 relaxation techniques as a probe to determine the specific molecular sites in metolachlor and acetanilide that interact with different dissolved and colloidal surrogate OM.

MATERIALS AND METHODS

Chemicals. ^{13}C-Labeled acetanilide (*ring*-$^{13}C_6$, *carbonyl*-^{13}C) was obtained from Isotec Inc. (Miamisburg, OH). Analytical grade nonlabeled metolachlor was obtained gratis from Ciba-Geigy Corp. with a purity of 99.0% and was used without further purification. The physical and chemical properties of acetanilide and metolachlor are listed in **Table 1**. The perdeuterated solvents deuterium oxide (D_2O) and methanol (CH_3OH-d_4) (each 99+% D) were purchased from Aldrich Chemical Co. (Milwaukee, WI) and Isotec, Inc., respectively. All solvents were used as purchased. Solutions of acetanilide were prepared in 100% D_2O and metolachlor in 60% D_2O and 40% CH_3OH-d_4. Nitrogen gas was used to remove the dissolved oxygen in solvents.

OM Surrogates. Commercial biopolymers that represent model input sources of OM were selected for this study. The biopolymers lignin (alkali) and cellulose were obtained from Aldrich Chemical Co., and chitin and collagen were obtained from Sigma (St. Louis, MO). The colloidal and dissolved OM solutions were prepared by sonicating the appropriate amount of solid biopolymer with D_2O for 15 min and filtering through a 1.0 μm glass fiber filter using a stainless steel filter holder. The OM solutions were bubbled with nitrogen to remove the dissolved oxygen. The solution total organic carbon (TOC) concentrations were measured using a Shimadzu 5000 analyzer with potassium biphthalate as a standard.

NMR Spectroscopy. The ^{1}H and ^{13}C NMR relaxation experiments in solution were conducted using a Bruker QE Plus spectrometer at 300 MHz for ^{1}H and at 75 MHz for ^{13}C. Proton spectra were acquired with a spectral width of 3300 Hz and 8192 data points. The ^{13}C NMR spectra were acquired using spectral widths of 7000 and 20000 Hz with 16384 data points. The ^{13}C NMR T_1 relaxation times were obtained using the standard inversion recovery Fourier transform (IRFT) and fast inversion recovery Fourier transform (FIRFT) pulse sequences $[PD-\pi_x-\tau-(\pi/2)_x-AT]_n$, where PD is the pulse delay, τ is the variable delay, and AT is the acquisition time. A pulse delay of 180 s with 16 scans and a recycle time of 12 s with 3000 scans were used for acetanilide and metolachlor, respectively, for the IRFT sequence. The FIRFT pulse sequence was used with a 14.0 s recycle time and 16 scans. Each T_1 array included 14 variable delay times (τ).

The ^{1}H NMR T_1 relaxation times were obtained using the standard IRFT pulse sequences for metolachlor. A pulse delay of 20 s with 16 scans was used with a set of 12 variable delay times. The chemical shifts were referenced against the residual proton signal of the deuterated solvent and tetramethylsilane (TMS) at 0 ppm. The NMR spectra were collected at 298 K and were controlled to $\pm$0.3 of set temperature. The T_1 relaxation times were determined using a three-parameter fit on the general expression for the NMR signal at time τ (*22*). The standard deviations were <1%.

After the T_1 relaxation times for the pure substrates in solution had been acquired, the OM was added to the NMR tube to complex with the substrate. Next, the T_1 relaxation times for the substrate complexed with the OM were determined. This procedure was repeated for each of the OM surrogates at a series of concentrations. The sample pH was measured using an Aldrich combination electrode.

RESULTS AND DISCUSSION

The ^{13}C and ^{1}H NMR T_1 relaxation times of the individual molecular sites of acetanilide and metolachlor were determined by gradually varying the total organic carbon (TOC) concentration of the OM from 0 to 240 ppm. Previous studies have found negligible changes in viscosity within this TOC concentration range (*23*). It was not possible to assign systematic changes of T_1 at the individual molecular sites at higher TOC concentrations because selectivity for individual sites was lost. Within the TOC concentration range used in these experiments, no significant changes in pH were observed between the OM free samples and those which contained OM (acetanilide, pH ~8.6; metolachlor, pH ~8.8). Therefore, the observed changes in T_1 relaxation times of acetanilide and metolachlor are not attributable to changes in pH or viscosity.

The chemical structures of the OM used had variable functional group identities and polarities. The elemental analyses of the OM are reported elsewhere (*4*, *6*). The calculated polarity index (PI) (O + N/C) of the OM in order of increasing polarity is 0.54 (lignin), 0.63 (collagen), 1.01 (chitin), and 1.11 (cellulose). The primary functional groups of the OM surrogates were confirmed experimentally by ^{1}H NMR and Raman spectroscopy. Nonpolar aliphatic and aromatic groups plus polar R−OCH_3 and R−OH groups were present in lignin. The −NH and C═O groups contribute to the polarity of collagen and chitin. Heterocyclic hexose rings and R−OH groups explain the polarity of chitin and cellulose. In the proceeding sections we describe the interaction between structurally very different forms of OM with metolachlor and acetanilide.

Relaxation Measurements of Acetanilide. The ^{13}C NMR T_1 relaxation times of the different aromatic sites and the carbonyl carbon of acetanilide-$^{13}C_7$ (*ring*-$^{13}C_6$, *carbonyl*-^{13}C) were determined. In the absence of any ligand, the T_1 relaxation times of the individual nuclear sites of the acetanilide molecule showed large differences. At the ortho, meta, and para aromatic sites (C-2, 6; C-3, 5; and C-4), respectively, T_1 varied from 2 to 4 s, whereas the T_1 at the ArCN (C-1) site was 20 s. The T_1 of the carbonyl carbon (C-7) was 33 s.

Acetanilide and Lignin. Figure 1 shows the T_1 relaxation of acetanilide as a function of TOC concentration of lignin, collagen, chitin, and cellulose. To obtain a relative comparison of the change in T_1 relaxation at the individual molecular sites, the T_1 relaxations were normalized to the T_1 in the absence of any ligand ($T_{1(blank)}$). A continuous decreasing trend in T_1 of all the individual sites of acetanilide was observed with an increasing lignin concentration (**Figure 1a**). The C-1 and C-7 carbons exhibited the highest relaxation rate at any given TOC concentration of lignin.

These observations can be explained by two possibilities: (1) relaxation mechanisms of the C-1 and C-7 quaternary carbons different from those of the other carbons due to the absence of attached protons and the direct influence of the OM; and/or (2) preferential interactions at C-1 and C-7 over the aromatic sites with lignin. The higher relaxation rate observed at the para C (C-4) suggests that the aromatic sites of acetanilide are also

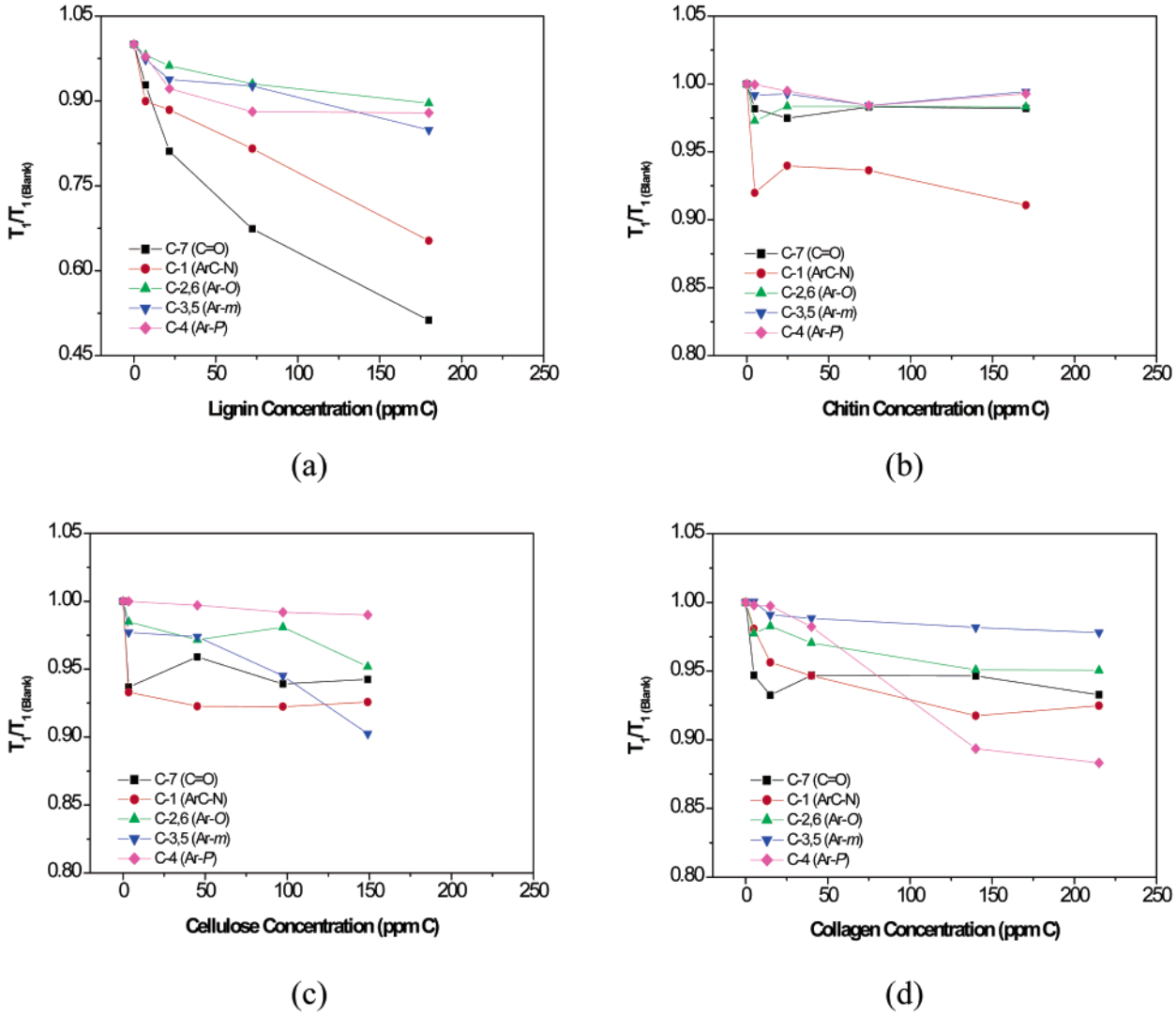


Figure 1. ^{13}C NMR T_1 relaxation of acetanilide individual sites in the presence of colloidal and dissolved organic matter in a 3.7×10^{-2} M solution: (a) lignin; (b) chitin; (c) cellulose; (d) collagen.

involved in interactions with the lignin. A relative upfield shift of the aromatic protons of acetanilide in lignin, indicating shielding due to interactions, also shows that the aromatic sites are involved in interactions.

Because the observed T_1 is an average of the acetanilide, which is interacting and non-interacting with the OM, the average molecular motion from exchange between associated and unassociated ligand would be expected to decrease continuously with TOC as observed in all of the molecular sites of acetanilide. This further suggests that the entire acetanilide molecule is involved in sorption. Thus, this observation indicates that sorption involves $\pi-\pi$ interactions between the aromatic groups, partitioning of acetanilide to the lignin, and possible H-bonding at the carbonyl and −NH proton.

Acetanilide and Chitin. In the presence of chitin an initial fast relaxation rate was observed at the C-1 carbon at TOC concentrations below 5 ppm and did not show any significant changes when the TOC was increased further until 75 ppm (**Figure 1b**). Small changes in relaxation were also observed initially at the carbonyl carbon (C-7) and at the ortho (C-2, 6) carbon. The para (C-4) carbon did not show any significant changes in relaxation initially.

These data indicate that the C-1 site was the most influenced by the primary binding site of acetanilide to chitin. We hypothesize hydrogen binding to the −NH proton occurs, the effects of which are felt at C-1 due to the delocalization of the electron density from the N atom to the aromatic ring that causes a partial double-bond character between the N and the aromatic ring at C-1. The ^1H NMR T_1 relaxation experiments of acetanilide in D_2O, to confirm this hypothesis with chemical shifts, were not conclusive because the −NH proton vanishes from the spectrum due to exchange with the deuterons. However, a downfield shift of the acetanilide −NH proton was observed in the presence of chitin, when the experiments were conducted in DMSO-d_6. This agrees with our hypothesis that −NH is the primary binding site of acetanilide to chitin and can be explained by the H-binding at the −NH proton. A decrease in the electron density at the −NH proton due to H-binding explains the downfield shift.

The change in T_1 relaxation time of the carbonyl carbon (C-7) was much less than that of C-1. This suggests that hydrogen binding or dipolar interactions to the carbonyl were less than those to the −NH. This also suggests that the polar functional groups of chitin most interacting with acetanilide are electron donors and most likely are the C═O groups of chitin.

Acetanilide and Cellulose. In the presence of cellulose, a fast relaxation rate was observed at both C-7 and C-1 at TOC concentrations below 5 ppm (**Figure 1c**). Because virtually no changes in T_1 relaxation of C-1 and C-7 were observed as the

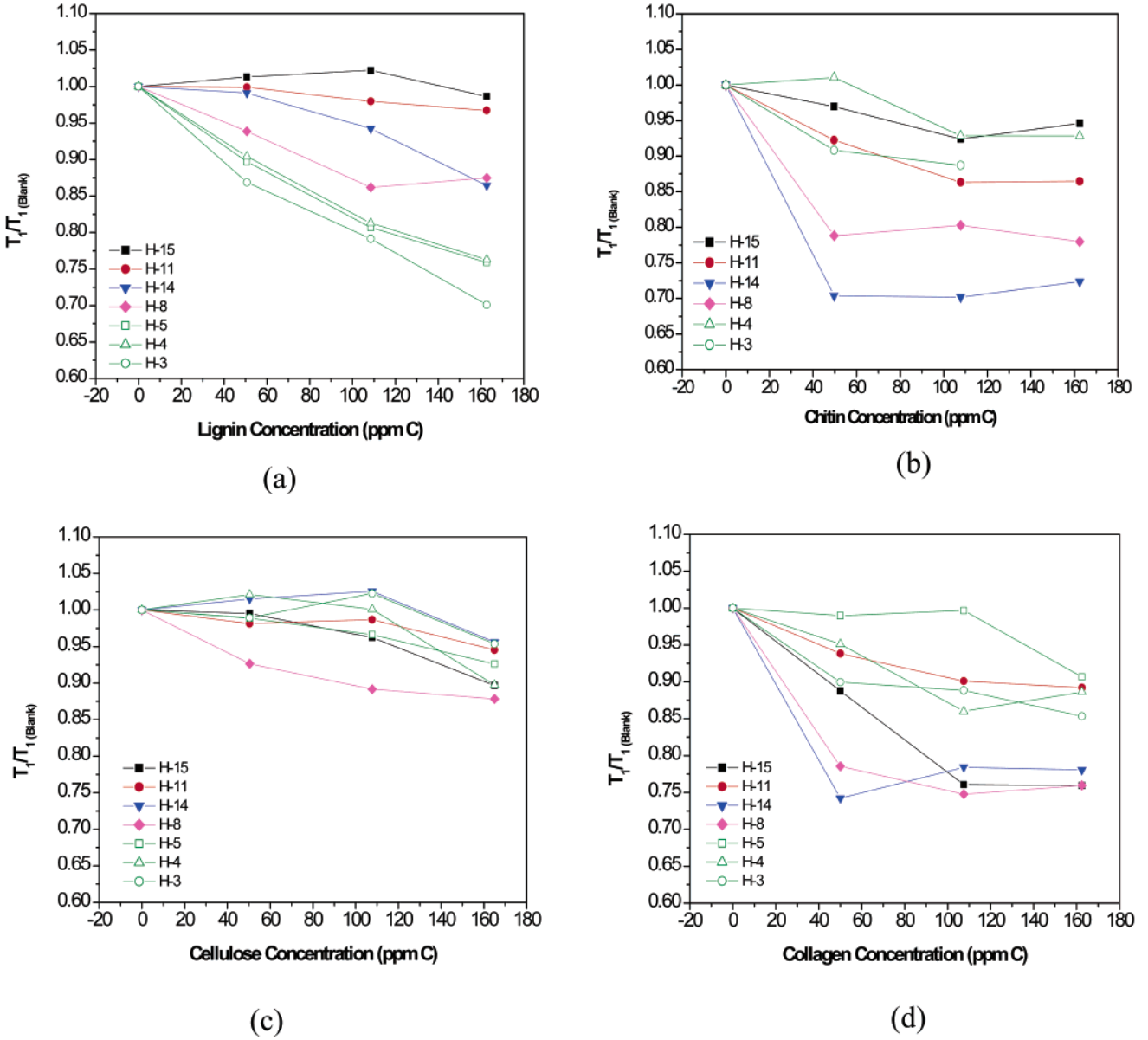


Figure 2. ^{1}H NMR T_1 relaxation of metolachlor individual sites in the presence of colloidal and dissolved organic matter in a 1.8×10^{-2} M solution: (a) lignin; (b) chitin; (c) cellulose; (d) collagen.

TOC concentration was increased further, no additional interactions are involved. Small changes in T_1 relaxation were observed at the ortho (C-2, 6) carbon, but the para (C-4) carbon did not show significant changes in T_1.

The specific interactions that influence the C-1 and C-7 carbons are the preferred interactions of acetanilide with cellulose (**Figure 1c**). The downfield chemical shift observed at the −NH proton, as in the case of chitin, supports H-binding at the −NH proton. The decrease in the relaxation rate of the carbonyl carbon (C-7) indicates dipolar interactions or H-binding to the carbonyl.

Acetanilide and Collagen. In the presence of collagen, an initial decrease in the T_1 relaxation time was observed at the C-7 and C-1 carbons (**Figure 1d**). The C-1 carbon relaxation rate at low collagen concentrations was less than that of cellulose or chitin at the same low concentrations. However, the relaxation at C-1 continually increased until 140 ppm. The ortho carbons, C-2, 6, also showed a similar increase in the relaxation pattern. No significant changes were observed above a TOC of 140 ppm. This indicates that the C-7 and C-1 of acetanilide are initially involved in specific interactions with the collagen.

The T_1 relaxation time of the para carbon, C-4, decreased after a TOC concentration of ~25 ppm was added. This unusual behavior of the C-4 relaxation in the presence of collagen shows that at higher TOC concentrations, the molecular sites of collagen also influence the aromatic carbons of acetanilide.

Relaxation Measurements of Metolachlor. The ^{1}H NMR T_1 relaxation times at the different molecular sites of metolachlor were determined as a function of TOC concentration using the same technique for acetanilide. Similar results were observed except as noted below. Because nonlabeled metolachlor was used, ^{13}C NMR T_1 relaxation experiments were not conducted with all of the OM surrogates due to the long experimental times required to obtain each T_1 value. However, the same relaxation trend was observed with both ^{1}H and ^{13}C NMR at the molecular sites of metolachlor, when lignin and chitin were used as the TOC source. **Figure 2** shows the ^{1}H NMR T_1 relaxation of different molecular sites of metolachlor in the presence of various OM surrogates.

Metolachlor and TOC. The aromatic protons of metolachlor (H-3, H-4, and H-5) showed higher relaxation rates versus the

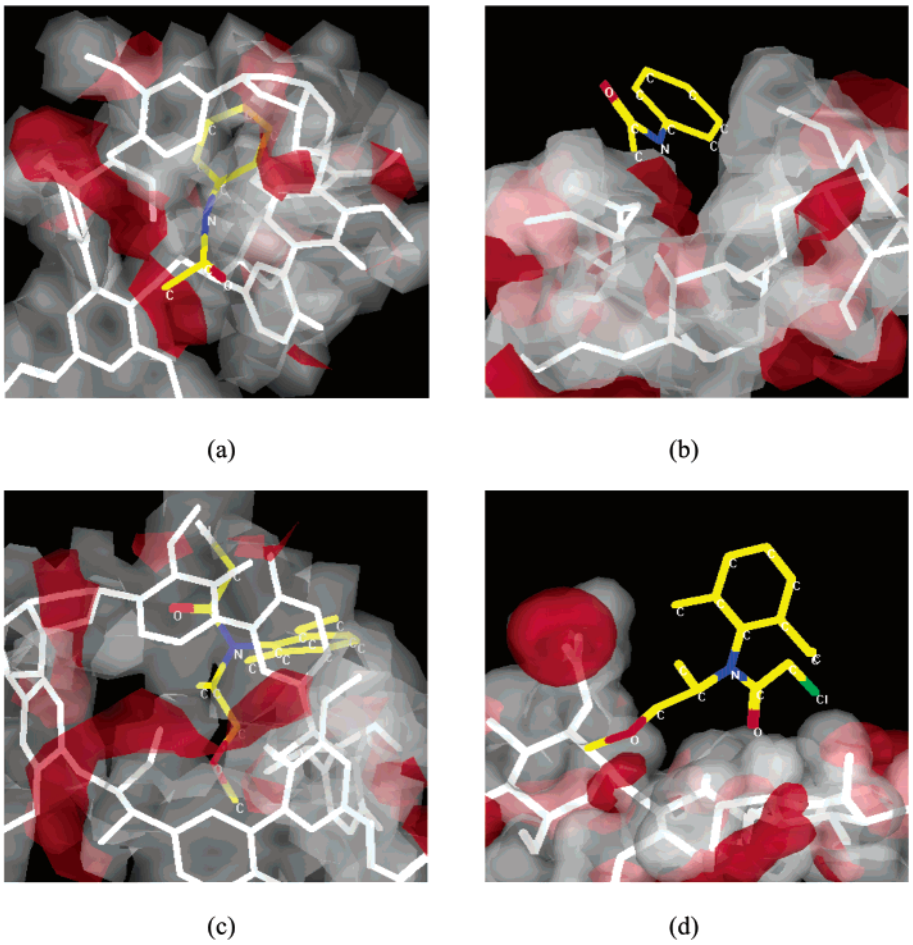


Figure 3. Predicted interactions and possible orientations of acetanilide and metolachlor on lignin and chitin: (a) acetanilide–lignin; (b) acetanilide–chitin; (c) metolachlor–lignin; (d) metolachlor–chitin.

alkyl protons as the TOC concentration of lignin was increased from 0 to 160 ppm (**Figure 2a**). For example, the initial relaxation rate of the H-8 protons was almost half of that of the aromatic protons. This suggests that the lignin preferentially interacted with the aromatic sites of metolachlor initially. The ^{1}H NMR spectra showed upfield shifts and line broadening of the aromatic and isopropyl protons of metolachlor. The T_1 of the individual protons continuously decreased with TOC concentration, indicating that the corresponding molecular motion of the same sites in metolachlor continuously decreased with TOC. This indicates $\pi-\pi$ interactions and partitioning of metolachlor to the lignin. The decrease in T_1 together with a downfield shift of the H-8 protons, due to electron withdrawal from these protons to the adjacent carbonyl (C=O), also shows H-binding-type interactions between the C=O and lignin functional groups.

When metolachlor interacted with chitin, the H-14 and H-8 protons showed higher initial relaxation rates than the aromatic protons (**Figure 2b**). This indicates that the preferential interaction sites of metolachlor with chitin were close to H-14 and H-8, hence reducing their time-averaged mobility. A continuous decrease of T_1 as a function of increasing chitin concentration was not observed. The downfield chemical shift of the H-8, H-13, and H-14 protons indicate deshielding or electron withdrawal from these sites (data not shown). A downfield shift of the aromatic protons also indicates electron withdrawal from the aromatic ring by the amide. These data suggest that the carbonyl and the isopropyl methyl ether oxygen of metolachlor interact with chitin through H-bonding or dipole−dipole interactions.

Metolachlor showed the least overall relaxation in the presence of cellulose (**Figure 2c**). The H-8 protons showed the largest change in relaxation times, indicating that these protons were the most influenced or closest to the preferential interaction site.

The largest change in T_1 relaxation was observed at H-8, H-14, and H-15 when metolachlor interacted with collagen (**Figure 2d**). The relatively fast relaxation of the H-15 protons of metolachlor in collagen compared to its relaxation in the presence of the other OM indicates restricted mobility of the total isopropyl ether substituent. As with chitin and cellulose, the nonaromatic sites of metolachlor preferentially interacted with collagen.

Interaction Sites and Orientation of Acetanilide and Metolachlor. When the changes in proton chemical shifts are compared, the aromatic protons of acetanilide showed the largest chemical shift in lignin followed by collagen (data not shown). Chitin, cellulose, and collagen induced larger changes in the chemical shift of the −NH proton signal than lignin. Comparatively, the more gradual decrease in T_1 at C-7 with lignin versus the sharp decline in T_1 at C-7 with cellulose and collagen indicates a weaker interaction with lignin. Furthermore, chitin did not show strong interactions to the C-7 or any of the aromatic sites except at C-1. **Figure 3** shows cartoon diagrams of the postulated interaction sites and the molecular orientations of an acetanilide molecule on lignin and chitin identified using T_1 relaxation data and ^{1}H NMR chemical shifts.

Figure 4 shows the change in the T_1 relaxation times of the aromatic para (H-4) proton and the nonaromatic H-8 protons

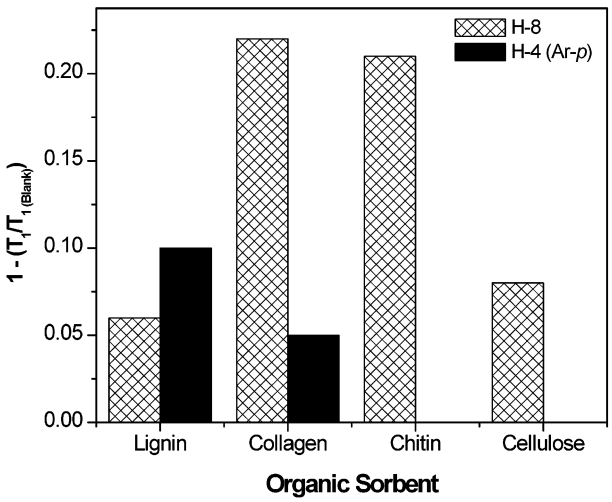


Figure 4. Change in the T_1 relaxation times of an aromatic (para) (H-4) and a nonaromatic proton (H-8) of metolachlor when interacting with different organic sorbents at a TOC concentration of 50 ppm. A value of "0" indicates "no change" in the T_1 relaxation time, that is, "no interactions".

(adjacent to the carbonyl) of metolachlor at a TOC concentration of 50 ppm. Changes in T_1 relaxation times were observed for the H-4 and H-8 protons, indicating that interactions were occurring at both the aromatic and H-8 sites of metolachlor with lignin. The change in the H-8 protons of metolachlor was higher than the aromatic proton when interacting with the more polar sorbents, collagen, chitin, and cellulose. The aromatic sites of metolachlor were not the preferred interaction sites with these more polar sorbents. The changes in ^{1}H NMR chemical shifts complemented the T_1 relaxation measurements at low TOC concentrations. The postulated interaction sites and orientations of a metolachlor molecule on lignin and chitin using T_1 relaxation data and ^{1}H NMR chemical shifts are shown in **Figure 3c**,**d**.

***T*$_1$ Relaxation and Organic Carbon Referenced Association Constants (K_{oc}).** The T_1 relaxation rates of the individual molecular sites of metolachlor and acetanilide were used to determine whether a relationship exists between the extent of binding and relaxation rates. K_{oc} values for metolachlor and acetanilide were determined using the following correlation for acetamide pesticides, developed from experimental data (*4*), where K_{ow} is the octanol−water distribution coefficient, C_w is the solubility in water, and PI is the polarity index [(O + N)/C] of the sorbent.

$$\log K_{oc} = 3.53 + 0.553 \log K_{ow} - 0.091 \log C_w - 3.51\ \mathrm{PI} \quad (1)$$

The T_1 relaxation of the aromatic sites of metolachlor showed better relationships with K_{oc} than the nonaromatic sites. **Figure 5** shows the changes in T_1 relaxation of the H-4 and H-8 protons of metolachlor and the C-1, C-4, and C-7 carbons of acetanilide when plotted against the K_{oc}. In metolachlor the change in T_1 of the H-4 proton followed the same trend as the change in the PI of the OM with K_{oc} (**Figure 5a**). The C-4 (para) carbon of acetanilide also showed a similar trend but was less prominent than the H-4 relaxation of metolachlor (**Figure 5b**). However, poor correlations were observed between the relaxation rates of the nonaromatic molecular sites such as the H-8 (close to C═O) and the C-7 (C═O) and K_{oc}. This suggests similarities in the interaction mechanisms of the aromatic molecular sites but different interaction mechanisms with the nonaromatic sites of metolachlor.

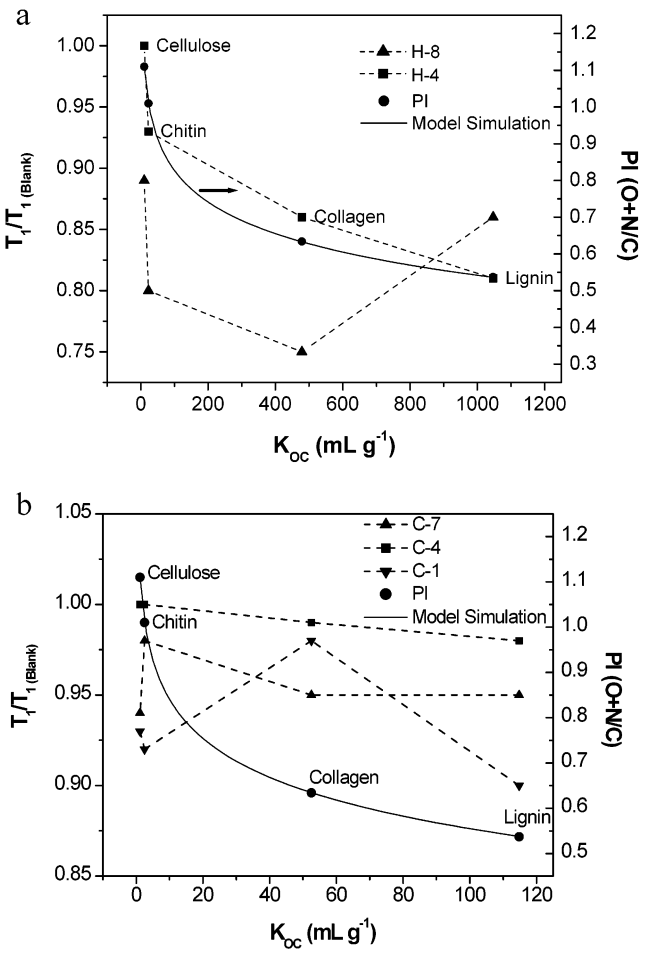


Figure 5. Relationship between T_1 relaxation and organic carbon referenced partition coefficient (K_{oc}) for (a) metolachlor and (b) acetanilide. Model simulation of the PI K_{oc} was done using eq 1.

Our results also clearly show that a direct measure of a steady-state association constant between a substrate and an organic sorbent cannot be always determined by measuring the changes in the relaxation time of any single nonaromatic molecular site such as at a quaternary carbon or a carbonyl carbon. The T_1 relaxation rate identifies the predominant type and sites of interactions occurring between specific pollutants and individual OM compositions.

Conclusions. Acetanilide pesticide interactions with OM surrogates were examined using ^{13}C and ^{1}H NMR spin−lattice relaxation techniques. Changes in T_1 relaxation times at multiple molecular sites of metolachlor and acetanilide with OM concentration were measured to identify the preferred interaction sites and/or interaction surfaces of the molecules with different OM surrogates. Interactions of metolachlor and acetanilide molecules with OM macromolecules resulted in a faster relaxation rate of those nuclear sites near the part of the molecule in the sorbate−OM complex. This allowed the identification of the possible interaction sites of the pesticide molecules and an approximate mapping of the molecular orientations on the OM surface. The specific interaction sites of a pesticide and its molecular orientation on the surface can influence its biodegradation properties as well as its exposure to soil organisms and resulting toxicity. Metolachlor and acetanilide showed more specific, high-affinity interactions at the nonaromatic sites with cellulose, chitin, and collagen. In contrast, their interactions with lignin occurred with less site specificity and involved both aromatic and nonaromatic sites. The relaxation measurements

also allow us to postulate the possible types of interactions that can occur between the acetanilide pesticides and different sorbents rich in specific OM surrogates. Further research must be conducted in more complex OM such as in mixed systems of biopolymers and humic substances that more closely represent environmental systems. The results of this study show that relative changes in NMR spectroscopic parameters can be used to identify specific molecular interaction sites to enable the prediction of molecular orientations and interaction mechanisms of pollutants at the sorbent−water interface.

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